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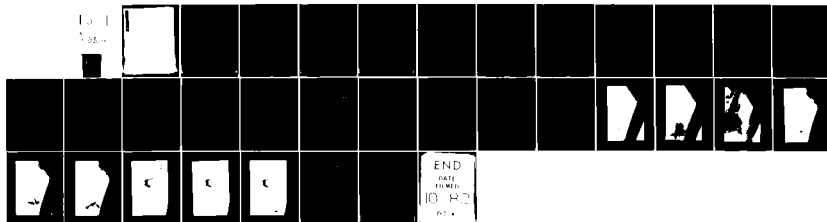
THE EFFECT OF ADDITIVES ON THE AEROSOLIZATION OF JP-5 JET FUEL.(U)

AUG 82 R C LITTLE, R PRATT, J B ROMANS

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20. ABSTRACT (Continued)

additive. In the case of each additive the MMD significantly increased with concentration at constant RPS. The effect of the Oppanol B-200 was comparable to that of FM-9 with respect to its influence on the MMD.

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THE EFFECT OF ADDITIVES ON THE AEROSOLIZATION OF JP-5 JET FUEL

I Introduction

Applied research has been underway for some time (1-3) to develop materials, called antimisting agents which when added to a jet fuel will inhibit the formation of highly dispersed droplets or mists. Interest in this area has increased greatly over the past 10 years to the point that a conference on antimisting fuels was recently held by the Federal Aviation Administration (4). Such antimisting agents presumably will greatly minimize the formation of ignitable air-fuel dispersions due to the lessened degree of atomization of the fuel-in-air mixtures - even in the presence of crash-related ignition sources. The mechanism by which these additives suppress the formation of mists remains a matter of conjecture. Furthermore, this situation is confused by the fact that most of the additives which have been studied are proprietary materials with no information available on structure or even molecular weight. However, interesting analogies appear between this dispersion phenomenon and other phenomena such as cavitation suppression and especially drag reduction. That is, those agents which have been found to exert a drag reducing effect have also exerted an antimisting effect. A salient difference, however, lies in the range of the additive concentration used. In drag reduction, phenomenologically-active concentrations are in the parts per million range whereas in antimisting effects the required concentrations are of the order of several tenths of a percent.

There is good reason to believe that the same agents which would be active in drag reduction would also be active in antimisting (5). It would then follow that antimisting agents should possess the following characteristics: (a) good dispersibility in the fuel, (b) essentially linear structure and (c) high molecular weight. One of the leading contenders as an antimisting agent is a proprietary material designated FM-9, developed by ICI in England. No information is available as to its structure or molecular weight. Using such an agent alone as a probe would give little information on the effect of structure or molecular weight upon any antimisting effect. It was, therefore, decided to observe the proprietary material, FM-9, in parallel with a known drag reducing agent, polyisobutylene. Polyisobutylene, being a hydrocarbon and having a solubility parameter of 8.0, is expected to be an optimum match for Navy JP-5 jet fuel because of the closeness of parameters and similarity of chemical structure. Since the ignition of dispersed fuel below its flash point is expected to be related in part to its drop size distribution, it was decided to study the aerosolization of neat jet fuel and various concentrations of the two additives in the fuel through use of the May aerosol generator.

II Experimental

Materials

Five samples of polyisobutylene (PIB) were procured from two sources: Oppanol B-200 (Wyandotte Chemical Corp.) and the Vistanex series L-120, L-140, L-180 and L-200 (EXXON Corp). One of the samples (Oppanol B-200) was fully characterized by drag reduction and viscosity measurements. The Vistanex materials were claimed to have the approximate molecular weight range of one million to five million. FM-9, a proprietary product (ICI), was received as a finished solution in JP-5 jet fuel. The neat JP-5 jet fuel used for the experiments was obtained from Andrews Air Force Base, Md. The heptane used in the characterization of Oppanol B-200 was chromatographic grade.

Methods

1. Viscosity/Drag Reduction

Viscosity measurements were made in a Cannon-Fenske capillary viscometer type 100 set in a constant temperature bath maintained at $25^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$. Drag reduction measurements were made in an automated drag reduction apparatus. The apparatus and procedure have been previously described (6).

2. Drop Size Evaluation

Figure 1 is a schematic illustrating the experimental techniques and flow of information developed in the drop size experiments. The May aerosol generator (BGI Incorporated) was used to generate aerosol dispersions of jet fuel and additive-modified jet fuel as a function of rotor speed. A Teflon slide collected the output which was immediately placed on a microscope stage and photographed. From a knowledge of the enlargement ratio, the drop segment diameter was measured. The contact angle of the drop on the same Teflon surface was determined using a contact angle goniometer (Central Scientific Company). From the segment diameters and contact angles the free drop diameters were calculated (7). The relation

$$\begin{array}{ccc} D & = & ND \\ \text{free drop} & & \text{segment} \end{array}$$

where D = diameter

$$\text{and } N = 2 \left[\tan \alpha / 2 (3 + \tan^2 \alpha / 2) \right]^{-1/3}$$

and α = contact angle

was used for this purpose.

The contact angle of the jet fuel and its solutions did not vary significantly from 40°. Approximately 30 microdrops were measured in each run and histograms were developed from the data. The mass median diameters were determined on probability paper (which assumes a Gaussian distribution). A Texas Instruments TI-59 programmable calculator and printer were used to develop the histogram data and perform other necessary calculations.

3. Fuel Flammability Tests

a. Apparatus

A spinning disk atomizer was used to measure the mist flammability of jet fuels. The disk, patterned after one used by Mannheimer (8) was made of brass and measured 4 1/4 inches in diameter and 1/2 inch in thickness. It contained a cavity in the center, 1 inch in diameter and 1/4 inch deep. Four radial holes 0.078 inches in diameter and spaced 90° apart were drilled from the rim of the disk into the cavity. In operation, fluid delivered to the center of the cavity while the disk was spinning was dispensed by centrifugal force through the radial holes in the form of a mist.

The disk was mounted on the vertically oriented shaft of the drive motor as shown in the schematic diagram in Figure 2. A GAST Model 1AM air motor drive (10,000 rpm, max.) was used for safety reasons. A variable pressure reducing valve was used to control the speed of the air motor. Speed of the spinning disk was measured by a Pioneer DT 36 digital photoelectric tachometer with a remote pickup which focused on a piece of reflective tape attached to the surface of the spinning disk.

The spinning disk and drive motor were mounted in the center of an 18 inch square test stand or table with the disk about 1 - 1/2 inches above the flat aluminum top. Air discharge from the motor was directed beneath the solid top. The source of ignition was a propane burner located 12 inches from the center of the spinning disk and at the same level. The entire assembly was placed in the center of an open-top rectangular cinder-block enclosure measuring 4 1/2 by 5 1/2 feet. A camera was used to record the flammability characteristics of the various fluids under study.

The jet fuel was delivered to the spinning disk from a safe distance through 1/4 inch diameter copper tubing by means of a low shear positive-displacement syringe or pump, consisting of a vertically mounted cylinder and movable piston. A schematic of the arrangement of the syringe and accessories are included in Figure 2. The cylinder measured 3 1/4 inches in diameter and 5 1/4 inches long. Displacement of the fluid was accomplished by moving the piston at a very slow rate by a lead screw driven by a

gear motor through a variable ratio speed reducer. Speed of the gear motor was controlled by a HELLER Model S-30 motor control unit and was monitored by a recorder driven by a DC generator coupled to the gear motor. Limit switches on the lead screw determined the length of travel of the piston. The volume of fluid displaced during a single stroke of the piston was approximately 1470 ml. Means were provided whereby the fluid delivery line could be purged with compressed air when charging the system with a new fluid.

b. Procedure

Unless the fluid to be tested was the same as that used in the previous determination, the fluid delivery line was purged by opening the air valve on top of the syringe cylinder. The filler plug was then removed and the piston lowered to the bottom of the stroke. The cylinder was then charged with the new fluid and the plug replaced.

It has been found beneficial in terms of disk speed stability to operate the air motor at half speed for several minutes while preparing for the first test of the day. The propane burner was then ignited, the disk drive motor brought up to the desired speed and allowed to stabilize for a few minutes. After the camera was in place, the syringe drive motor was started. The delivery rate of the fuel was 400 ml/min.

As the fluid entered the cavity in the center of the spinning disk, it was found that the disk speed was reduced 12-13% at 400 ml/min delivery because of the centrifugal force required to disperse the fluid from the spinning disk. At this point, the operator had the option of restoring the disk to its original speed, or of raising the speed an appropriate amount before the test fluid was admitted to the disk in order to achieve the desired speed during the test itself. In either case, the same procedure was followed for a given series of tests; for, in general, it has been found that higher disk speeds tended to increase the flammability of the fluid under test. This is probably due to the formation of smaller droplets at the higher disk speeds for a given fluid. Similar behavior has been observed (9) with the May spinning disk aerosol generator.

Any propagation of yellow flame away from the blue propane flame was considered evidence of ignition of the fluid under test. As ignitability increased, an arc of flame was established which sometimes completely encircled the spinning disk. The degree of encirclement at a given disk speed was a qualitative indication of the relative flammability of the fluid. The flame could be extinguished by stopping the syringe drive motor. If there was no propagation of flame from the propane flame, the fluid under test was considered to be non-flammable under the conditions of the test.

III Experimental Results

Viscosity and Drag Reduction

Figure 3 reports measurements made in the capillary viscometer for the purpose of estimating the molecular weight of the Oppanol B-200 sample. The solvent used, heptane, with its solubility parameter (δ) of 7.45 is neither a good nor poor solvent for polyisobutylene ($\delta = 8.0$). A least squares plot of reduced viscosity versus concentration in grams per deciliter was made yielding an intrinsic viscosity, (η) , of 5.21 dl/g. The data conformed to Huggins' equation but the Huggins constant seemed somewhat high ($K = 1.09$). The molecular weight of the PIB was determined from the Mark-Houwink relation estimated for PIB in heptane, $(\eta) = 7.57 \times 10^{-5} M^{0.75}$. The value of the exponent in the relation was approximated from Van Krevelen and Hoftyzer's work (10) and the value of K from Fox and Flory's relations (11). A molecular weight of 2.8×10^6 was obtained for the Oppanol B-200 sample.

The Oppanol B-200 sample also showed substantial drag reduction characteristics. Figure 4 shows a drag reduction plot designed to determine the drag reduction index (12,13). A linear plot of concentration divided by fractional drag reduction versus concentration (expressed in ppm) yields an index of 0.388 for $DR_m/(c)$ (or 38.8 based on percent drag reduction) where DR_m is the maximum drag reduction and (c) is the intrinsic concentration (14). From the plot of DR_m/c versus molecular weight determined for Polyox polymers in water (13), this index would correspond to a polyethylene oxide polymer of 2.4×10^6 in molecular weight. Since drag reduction is probably polymer length related, the equivalent length for a polyisobutylene molecule would correspond to a molecular weight of 3.0×10^6 , an excellent check of the intrinsic viscosity results.

It has been conjectured that both the drag reduction and antimisting effects are the result of viscoelastic phenomena. Compounds which are good drag reducing agents also seem to be good antimisting agents (4) in spite of the fact that drag reduction occurs in the parts per million range of concentration whereas antimisting appears to take place in the tenths of a percent concentration range. Drag reduction of a polymer solution when referred to the pure solvent tends to decrease as the polymer concentration increases because of increased viscous drag of the solution over the solvent. However, if the solution is referred to a non-Newtonian fluid having the same power law indices (but non-drag reducing in nature) a different rating is obtained. Figure 5 shows the results of this exercise. In this plot the percent drag reduction of the polymer solution has been referred to a non-drag reducing fluid having the same power law

indices as the polymer solution. The percent drag reduction for the polymer solution data is seen to remain sensibly constant over a very wide range of polymer concentrations i.e., up to 1000 ppm or 0.1%. Thus drag reduction effects persist into the antimisting regime and do not seem reduced by increases in solution viscosity (or polymer concentration).

Mass Median Diameter Determination

Jet Fuel, JP-5

The method outlined in the experimental section for the determination of droplet sizes is an approximate one. Although every attempt was made to shorten intervals between microdrop collection and microphotography, there existed the dual possibilities of evaporation during micro-drop production/collection and of coalescence of adjacent droplets resting on the slide before the photographs were taken. The sample size taken for counting, typically thirty microdrops, is a minimal statistical sample. Moreover, the use of a log normal distribution to estimate the mass median diameter may not always be the most appropriate analytical technique (15) although it is commonly used. However, if the analyzed data are used to look at relative rather than absolute changes in drop size, as produced by the addition of high molecular substances to the subject fluid, then at least qualitative effects may be assessed.

Figure 6 is a plot of diameter in micrometers versus the cumulative weight percent and cumulative frequency percent from the histogram data (Fig. 7). The driving pressure for the May aerosol generator was 6 psi which corresponds to a rotational velocity of 828 revolutions per second or a tangential velocity of 152 mph. Such a velocity is to be encountered in the landing speed of high performance aircraft. The estimate of mass median diameter (MMD) from the plot was 20 μ m. The median diameter corresponding to a cumulative frequency percent plot, on the other hand, was 15 μ m. Direct calculation from the histogram data led to a weight-average value of 24 μ m and a number-average value of 28.5 μ m for the respective median diameters. Because of the popularity of cumulative weight percent plots and the use of the data to show relative rather than absolute effects, it was decided to use the cumulative weight percent plots as a means of evaluating the data. The effect of increased rotor speed on the mass median diameter is reported in Table 1 where the mass median diameter has been tabulated with respect to rotor speed in revolutions per second (RPS). The decrease in MMD with rotor speed is quite evident. Velocities lower than 828 RPS (152 mph) were not possible since rotor instability developed.

Mass Median Diameter of PIB Solutions in JP-5

Effect of Velocity Concentration and Molecular Weight

The action of the May generator on the Oppanol B-200 solution would frequently produce a large microdroplet in which 25 to 60% of the photographed sample mass was concentrated. A distribution of microdroplets of lesser size would then be observed showing fewer large microdroplets followed by smaller microdroplets peaking somewhere between 25 to 75 μm depending upon the rotor speed. Figure 8 reports the data typically observed for a rotor speed of 828 rps. Fifty-five percent of the collected sample mass (as photographed) was concentrated in one microdroplet of 195 μm diameter. No microdroplets between 120 and 180 μm were observed. A median diameter of 40 μm is observed in the lower microdroplet range of sizes. Figure 9 plots the diameter versus the cumulative weight percent on logarithm probability paper. A mass median diameter of 110 μm was obtained. Two separate runs were made which appear to be consistent with approximately the same mass median diameter. A number of experiments were run at higher rotor speeds and this data is reported in Table 1. A decrease in mass median diameter for the Oppanol B-200 solutions is observed with increasing rotor speed. Also included in Table 1 are the mass median diameter data for the JP-5 neat fuel. The relative decrease in diameter for both solution and neat fuel is approximately the same as the rotor speed is increased.

Table 1 also reports the effect of Oppanol B-200 concentration on the MMD as a function of polymer concentration at selected rotor speeds. There is a distinct increase in MMD with increasing concentration. The first increments of polymer produce large effects in droplet size increase. The effect obviously decreases on a size per unit concentration basis as the concentration is increased. At 1 percent concentration of Oppanol B-200, the droplet reaches a volume size which is 1000 times greater than that of the neat fuel droplets. The effect of PIB molecular weight is reported in Table 2. At the working level of 0.25 percent polyisobutylene, large changes in additive molecular weight appear to produce somewhat larger microdroplets. For example, an increase in nominal molecular weight from 1 to 5 million changes the microdroplet diameter ratio of PIB solution to neat fuel from 3.8 to 5.8. Since volume ratio is the cube of the diameter ratio, the L-200 sample produces a microdroplet volume (at the mass median point) approximately 3.5 times greater than that of the L-120 sample.

Mass Median Diameter of FM-9 Solutions in JP-5.

Effect of Velocity and Concentration

The effect of FM-9 concentration and rotor velocity on mass median diameter is reported in Table 3. The FM-9 solution was supplied as a 0.3 percent concentration in JP-5. Lower concentrations of additive were obtained by appropriate dilution with neat JP-5. Upon comparing the FM-9 data with the PIB data it is evident that the mass median diameter decreases more rapidly for the FM-9 material than for the PIB as the concentration of additive decreases. Moreover, increasing rotor velocity has a much greater effect on the decrease of MMD for the FM-9 solution than for the PIB solutions at all concentrations. For example, the MMD of the 0.3 percent FM-9 solution decreased from 148 μ m at a rotor speed of 828 RPS to 32 μ m at 1533 RPS. The 0.25 percent PIB solution MMD, on the other hand, decreased from 110 μ m to 66 μ m under the same conditions. At higher rotor velocities, PIB-specifically Oppanol B-200 - appears to have the edge on FM-9. At lower rotor speeds, however, the FM9 and B-200 materials are roughly comparable in their effect on the MMD.

Ignition Tests

Early experiments with both marine distillate and with JP-5 aircraft jet fuels indicated that in order to achieve reproducible ignition and sustained burning in the flammability apparatus, a minimum fuel delivery rate of 400 ml/min and a spinning disk speed of about 5000 rpm were required. At disk speeds as low as 3300 rpm, JP-5 fuel was dispensed in readily observable discrete drops. Though the drops burned as they passed through the test flame, ignition was erratic, and as may be seen in Figure 10, no propagation of the flame occurred. Increasing the speed to 4900 rpm (61 mph disk tangential velocity) resulted in some propagation of the flame (Figure 11). However, as may be seen in Figure 12, if the disk speed was increased to 6400 rpm (80 mph tangential velocity) the flame nearly encircled the flammability apparatus. The experiment was repeated a number of times and established that this effect always occurred in the region of 6300-6400 disk rpm. It was of interest to find that once the encirclement of flame was established, the disk speed could be reduced to about 5000 rpm before the flame propagation was materially reduced.

The flammability apparatus was filled with JP-5 fuel containing 0.3 percent FM-9. Because of the inadvertent dilution with unremoved JP-5 fuel in the system, the concentration of the FM-9 mixture was about 0.2 percent. The test was started at a disk speed of 6400 rpm. As seen in Figure 13, the flame generated was confined to a small volume surrounding the propane test flame. At 8200 rpm, the volume of flame increased slightly (Figure 14). At the maximum disk speed of 10,000 rpm (125 mph tangential velocity), no propagation of flame occurred. As seen in Figure 15, the envelope surrounding the test flame appears

larger but this may be due in part to the windage effects from the higher speed of the spinning disk.

The FM-9 fuel was removed from the delivery system and the apparatus was thoroughly flushed with JP-5 fuel. Subsequent tests of the JP-5 fuel gave results identical with those obtained earlier. This indicated that any residual FM-9 fuel in the system had a negligible effect.

The JP-5 fuel was entirely removed from the system and replaced with 0.3 percent FM-9 in jet fuel. Flammability tests obtained were identical with those obtained with the more dilute 0.2 percent FM-9 fuel. This suggests that the concentration of this mixture may be reduced by one-third without adverse effects on the flammability.

The flammability apparatus was then thoroughly flushed with JP-5 fuel, the residual removed and the system filled with 0.2 percent polyisobutylene in marine diesel fuel. At a disk speed of 6500 rpm, no ignition occurred, though yellow scintillation effects appeared in the test flame (Figure 16). At a disk speed of 8000 rpm (100 mph tangential velocity), the yellow discoloration of the flame was increased slightly (Figure 17). Only a slight additional increase in the yellow flame volume is seen in Figure 18 where the disk speed was 10,000 rpm. By comparing the series of Figures 13, 14, and 15 with Figures 16, 17 and 18, it can readily be seen that the effect on the propane test flame by the fuel containing 0.2 percent polyisobutylene is less pronounced than that imposed by the FM-9 fuel. Some of this difference may have arisen from differences in the flammabilities of the base fuels. However, the fire-resistant properties of either of the antimisting fuel compositions are obvious when compared with neat JP-5 fuel.

IV Conclusion

1. The proprietary antimisting jet fuel additive, FM-9, greatly increases the mass median diameter of aerosolized jet fuel produced at the 0.2 to 0.3% concentration level and a rotor speed of 828 RPS.

2. Polyisobutylene (Oppanol B-200) of three million molecular weight is approximately equivalent to FM-9 in its effect on MMD at the 0.25% concentration level, at the low rotor speed.

3. Increasing rotor speed from 828 RPS to 1522 RPS causes the mass median diameter of aerosolized dispersions to decrease far more rapidly for FM-9 modified jet fuel than for fuel containing Oppanol B-200.

4. Increases in both concentration and molecular weight produce significant increases in the mass median diameter of additive-modified fuel.

5. The superior performance of polyisobutylene over FM-9 in its jet fuel dispersions suggests its application in cases where extremely high velocities might be encountered, for example as in unwanted fuel ingestion in jet engines.

6. The flammability tests for FM-9 and PIB dispersions in selected fuel samples validate the fire-resistant qualities of both additives at concentrations of 0.2% and 0.3%.

Acknowledgment

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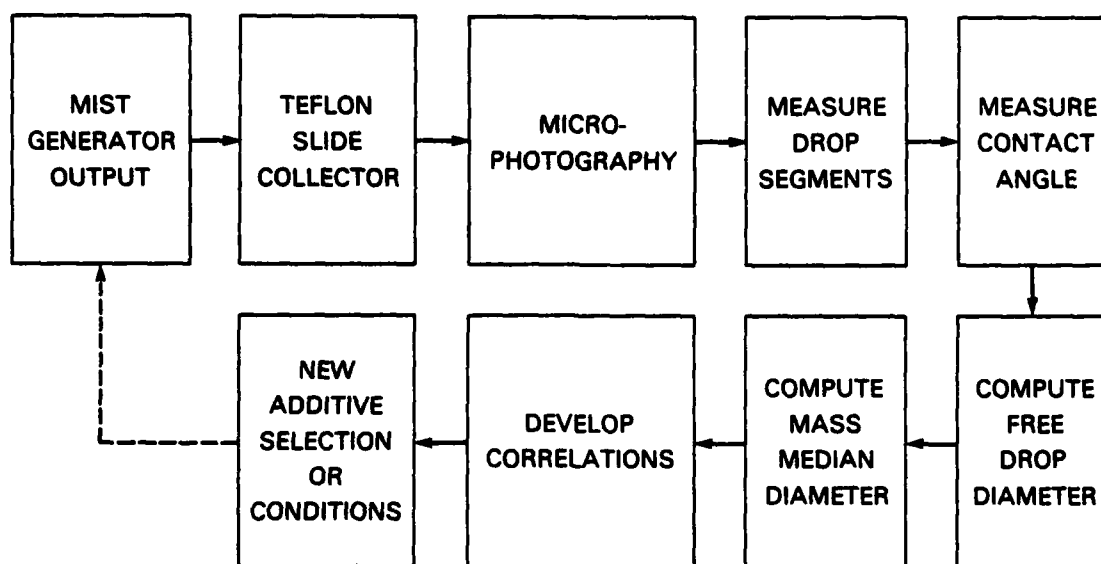


Fig. 1 — Information flow for drop size determination

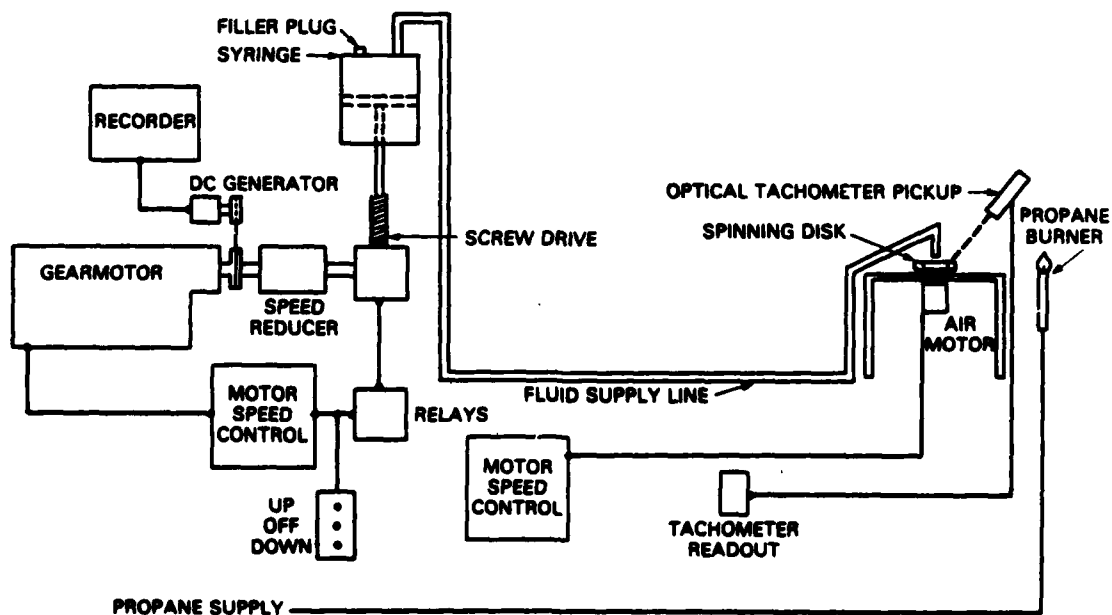


Fig. 2 — Flammability apparatus

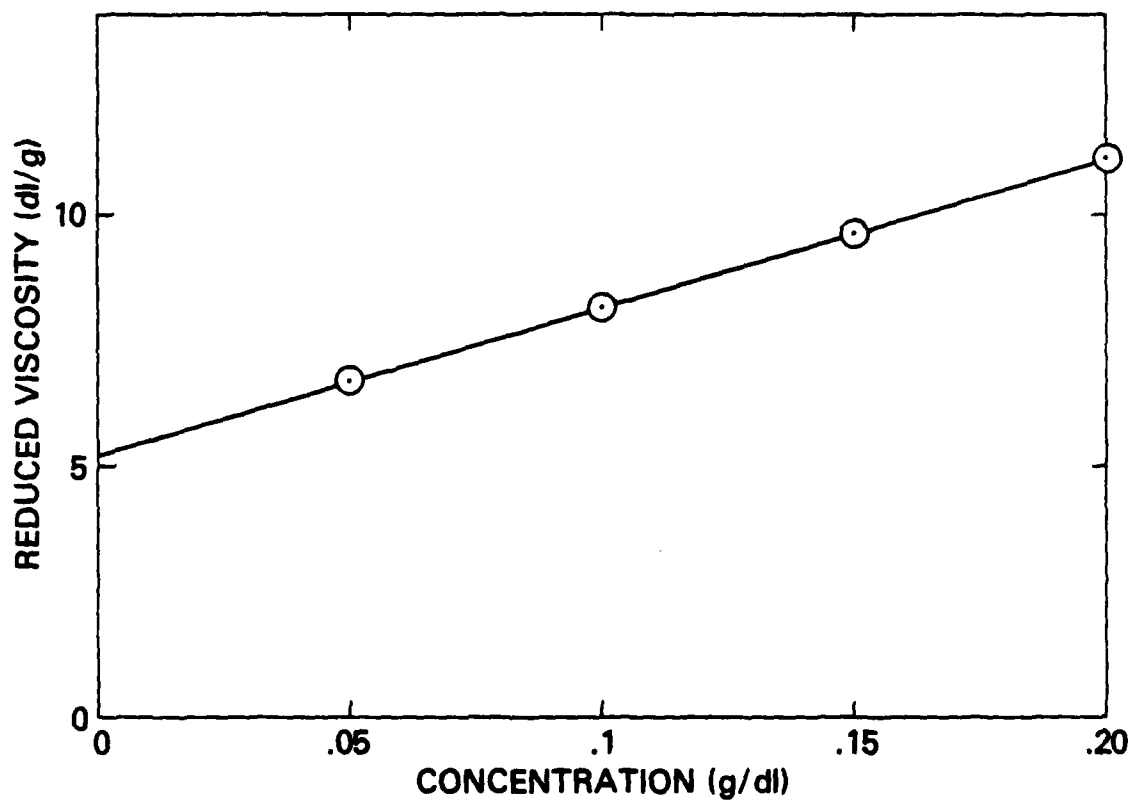


Fig. 3 — Reduced viscosity vs concentration for Oppanol B-200 solution at 25° C

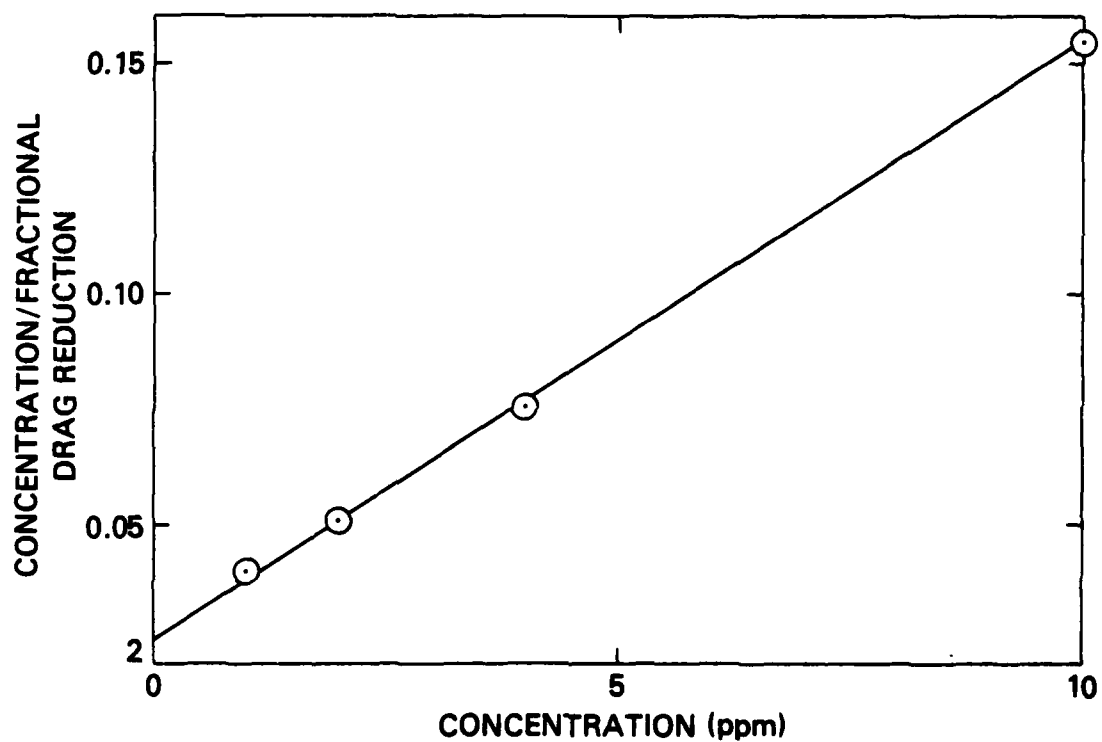


Fig. 4 — Drag reduction of Oppanol B-200 in JP-5 jet fuel

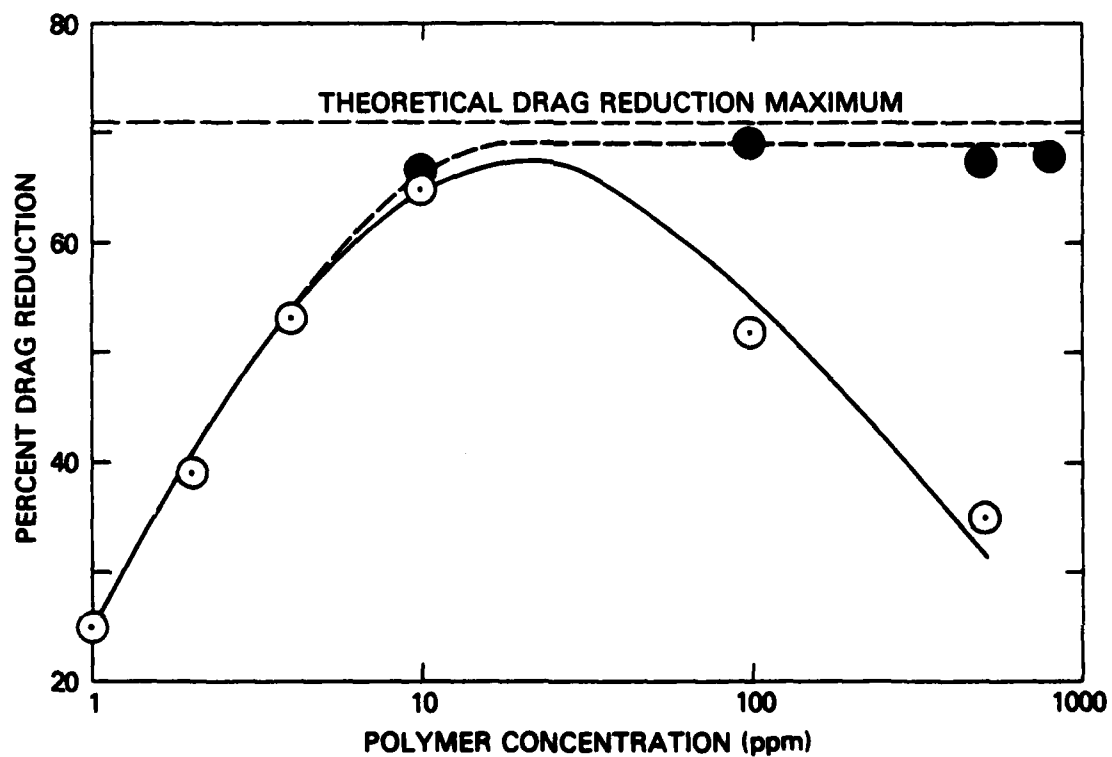


Fig. 5 — Drag reduction of Oppanol B-200 in JP-5 versus concentration
 ○ — drag reduction referred to solvent; ● — drag reduction referred to the non-drag reducing solution with same power law indices

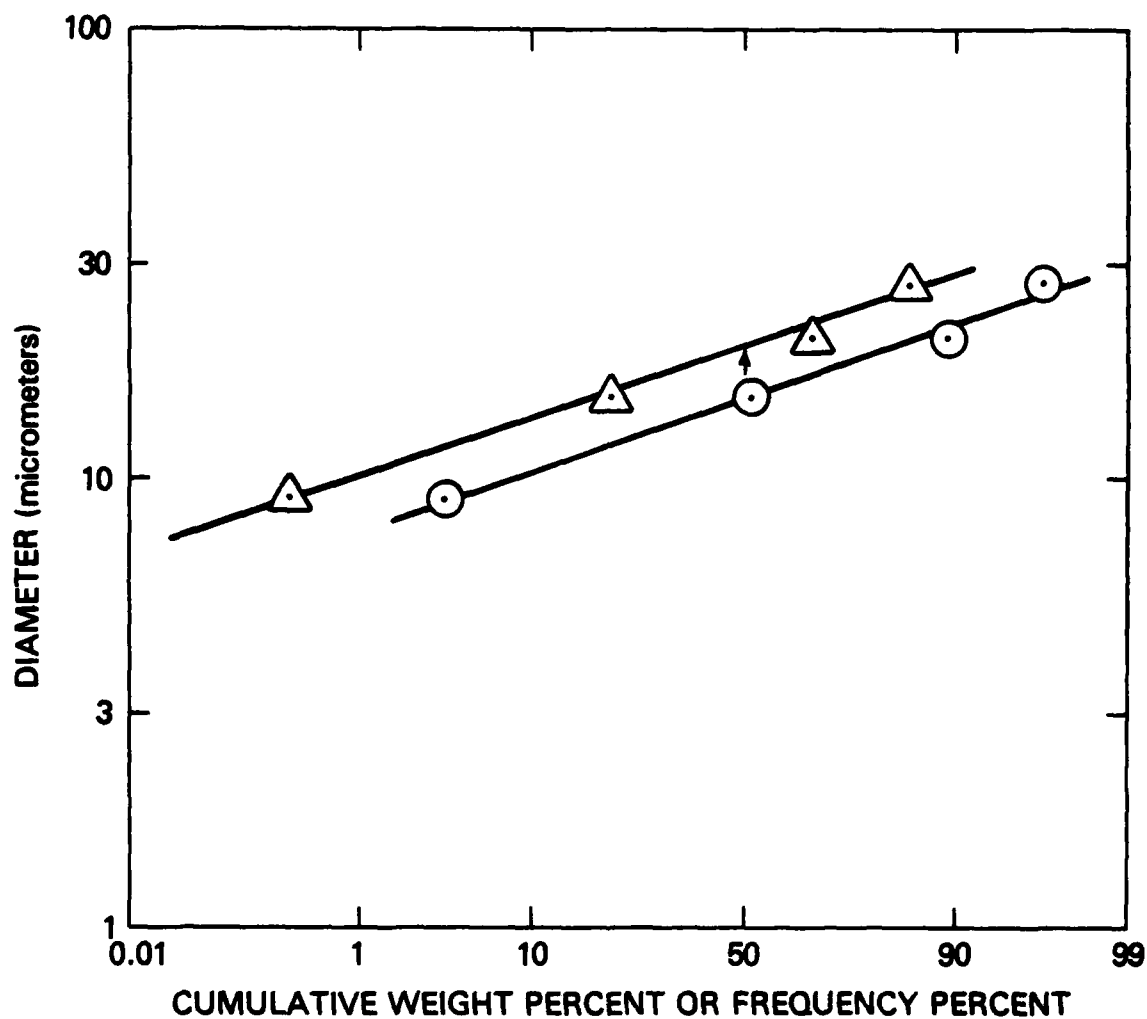


Fig. 6 — Probability plot of droplet size vs cumulative weight percent for 828 RPS in May Generator for JP-5 neat fuel; Δ cumulative weight percent, \circ cumulative frequency percent

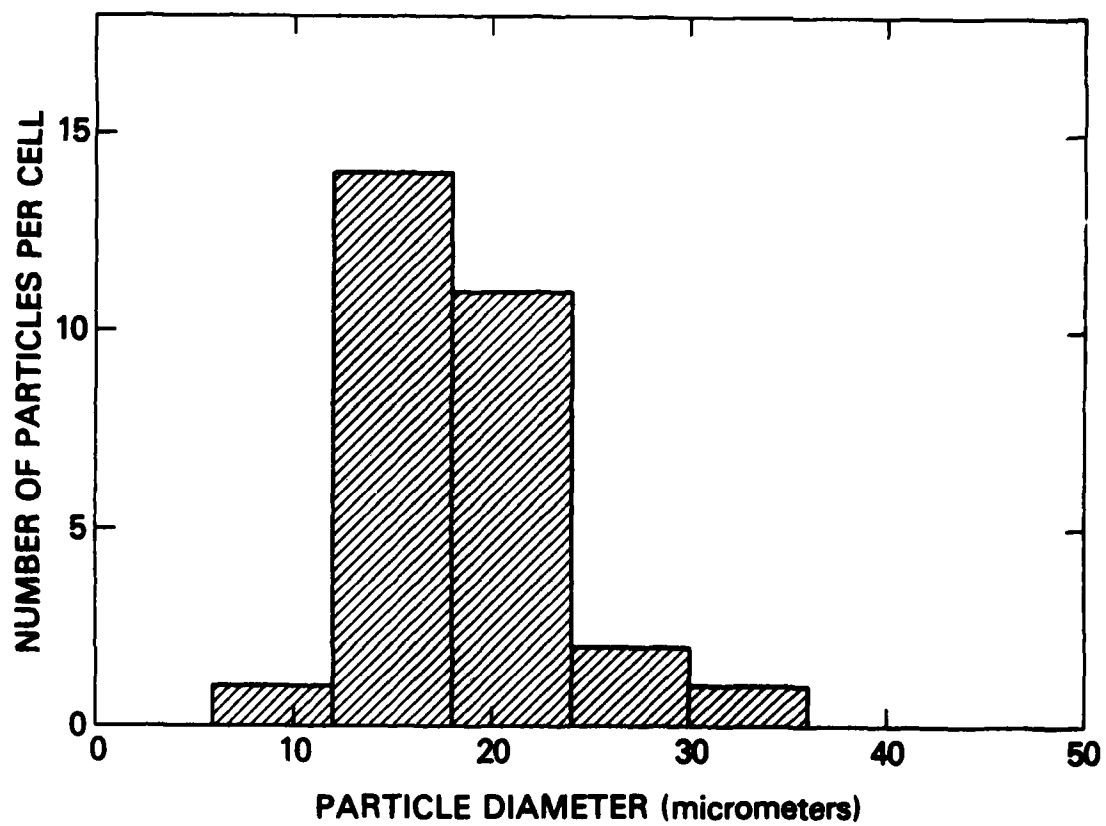


Fig. 7 — Histogram of droplet size for JP-5 neat fuel

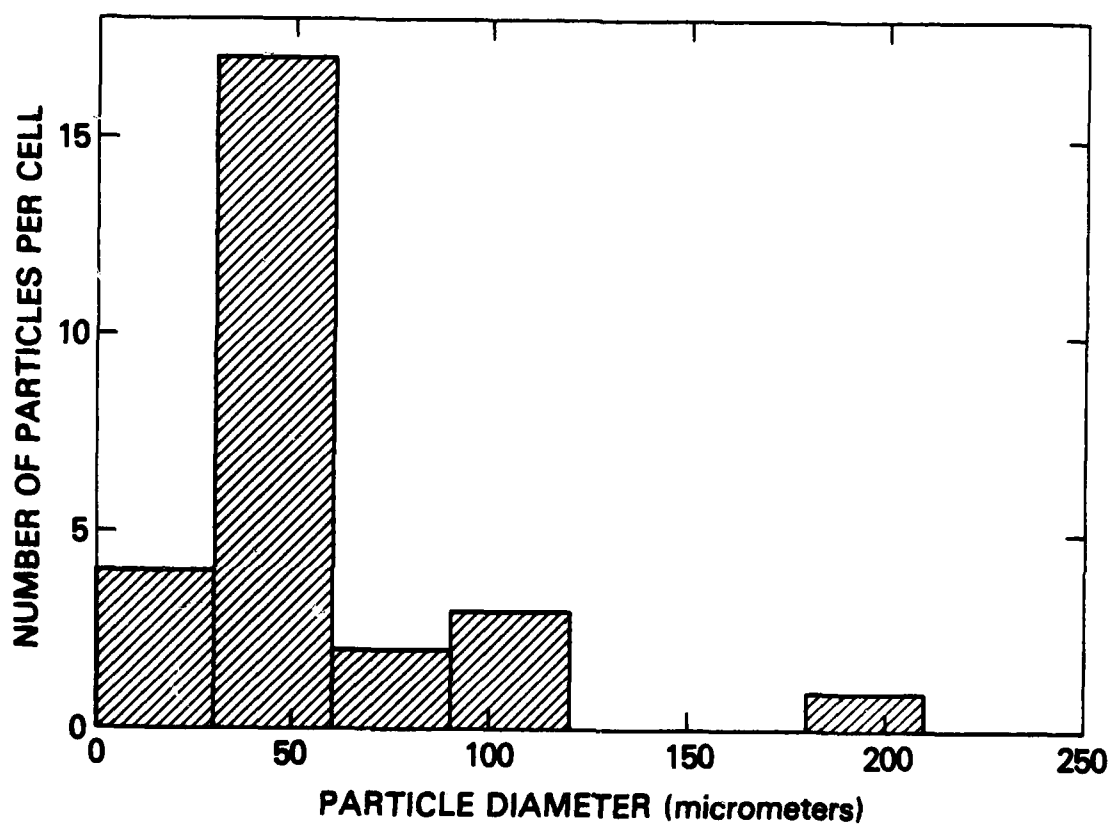


Fig. 8 — Histogram for 0.25 percent Oppanol B-200 in JP-5

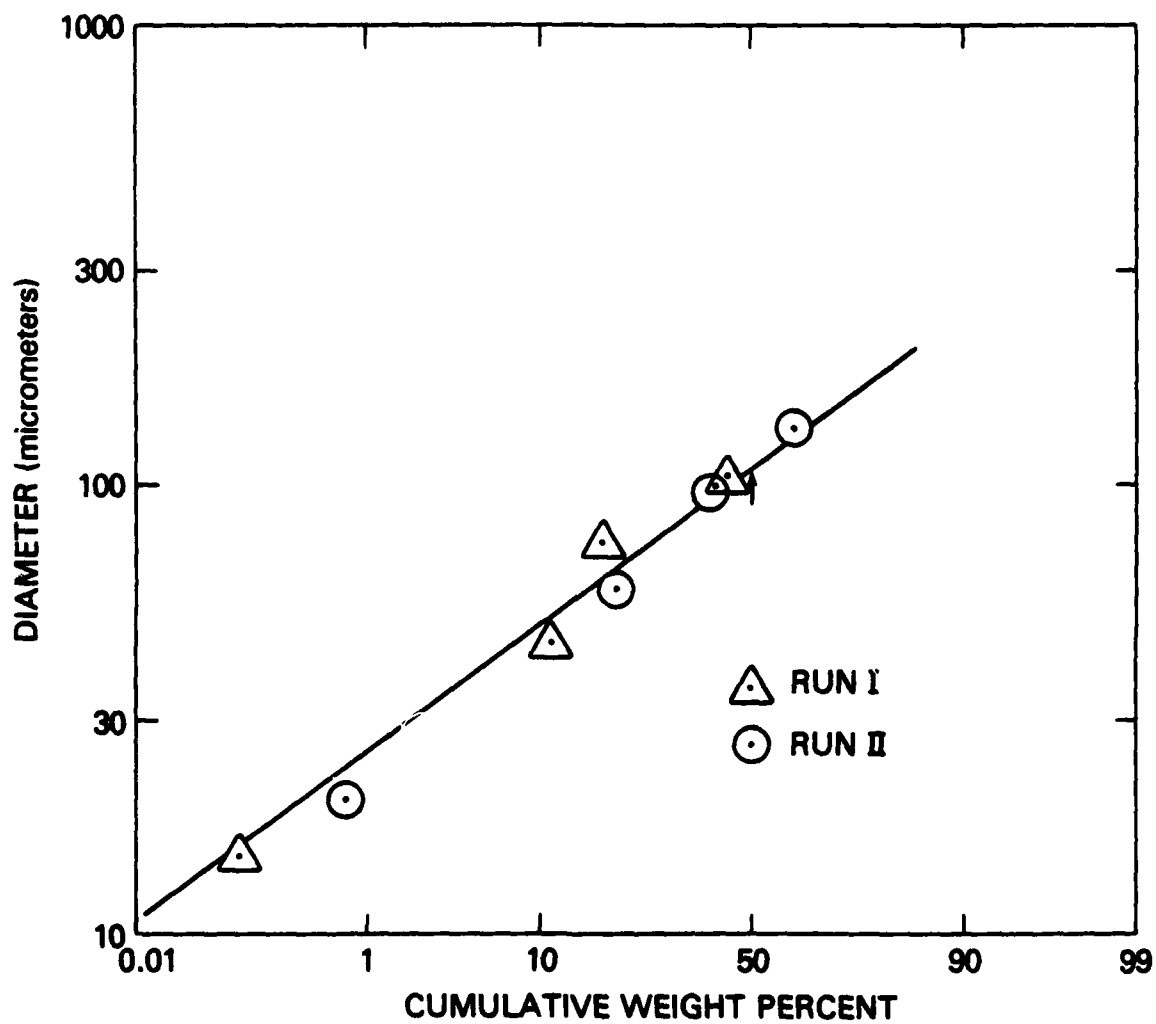


Fig. 9 — Probability plot of droplet size vs cumulative weight percent for 0.25 percent Oppanol B-200 at 828 RPS in May Generator; Δ Run I, ○ Run II



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Fig. 10 — JP-5 in flammability apparatus at 3300 rpm



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Fig. 11 — JP-5 at 4900 rpm



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Fig. 12 — JP-5 at 6400 rpm

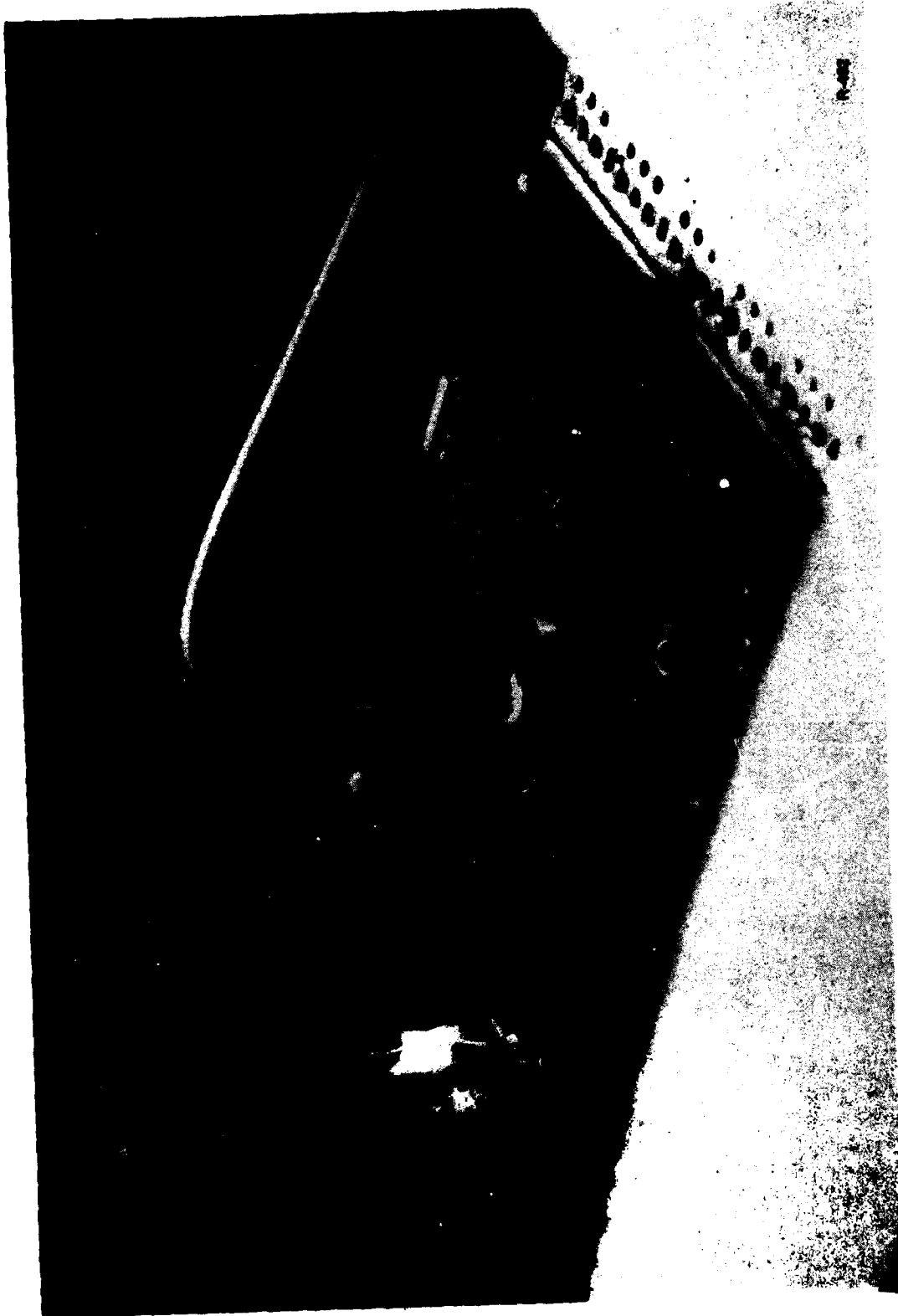


Fig. 13 — 0.2 percent FM-9 in JP-5 at 6400 rpm



Fig. 14 — 0.2 percent FM-9 in JP-5 at 8200 rpm



R-468

Fig. 15 — 0.2 percent FM-9 in JP-5 at 10,000 rpm



Fig. 16 — 0.2 percent Oppanol B-200 in JP-5 at 6500 rpm



Fig. 17 — 0.2 percent Oppanol B-200 in JP-5 at 8000 rpm



Fig. 18 — 0.2 percent Oppanol B-200 in JP-5 at 10,000 rpm

Table 1 — Effect of concentration and rotor velocity on mass median diameter of Oppanol B-200 solutions in JP-5

<u>Concentration, wt-%</u>	<u>Rotor Velocity, (RPS)</u>			
	828	985	1325	1533
	<u>MMD, μm</u>			
0	20	17	14	9
0.0625	80	70	—	52
0.250	110	93	73	66
0.500	175	138	—	120

Table 2 — Effect of Vistanex molecular weight on mass median diameter at constant rotor velocity (828 RPS) and concentration (0.25 percent)

<u>Vistanex Cpd.</u>	<u>Nominal Molecular Weight</u>	<u>MMD (μm)</u>	<u>Diameter Ratio PIB/JP-5</u>
L-120	1 x 10 ⁶	75	3.8
L-140	2 x 10 ⁶	84	4.2
L-180	3 x 10 ⁶	110	5.5
L-200	5 x 10 ⁶	115	5.8

Table 3 — Effect of concentration and rotor velocity on mass median diameter of FM-9 solutions in JP-5

<u>Concentration, wt-%</u>	<u>Rotor Velocity (RPS)</u>			
	828	985	1325	1533
	<u>MMD μm</u>			
0	20	17	14	9
0.05	23	22	20	16
0.15	62	29	22	21
0.20	110	84	32	25
0.30	148	96	38	32

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